November 18, 1880.

THE PRESIDENT in the Chair.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

General Boileau, Mr. Currey, Mr. De La Rue, Mr. Hudson, and Mr. Matthey, having been nominated by the President, were elected by ballot Auditors of the Treasurer's Accounts on the part of the Society.

The Presents received were laid on the table and thanks ordered for them.

The following Papers were read :—

I. "On the Essential Properties and Chemical Character of Beryllium (Glucinum)." By L. F. NILSON and OTTO PETTERSSON. Communicated by WARREN DE LA RUE, D.C.L., F.R.S. Received June 21, 1880.

In this paper we wish to call attention to some experimental facts which may give a clue to the real nature of beryllium, an element which since the beginning of this century has been the enigma of inorganic chemistry.

The oxide of beryllium was discovered in 1795 by Vauquelin. It was considered a monoxide, BeO, until 1815, when Berzelius* ranged it, principally on account of its basic sulphates, among the sesqui-oxides. The weighty reasons for this arrangement, never since refuted, which Berzelius added later in the fifth edition of his "Lehrbuch d. Chemie," p. 1225, are too well known to be recorded here.

In 1842 Awdéeff † analysed the double sulphates and fluorides of beryllium, which showed qualities not agreeing entirely with the analo-gous compounds of aluminium, iron, chromium, &c. As the formula of these compounds could be written

$$\text{KO,SO}_3 + \text{BeO,SO}_3,$$
$$\text{KFl} + \text{BeFl},$$
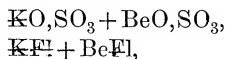
this was considered by the chemists of that time to support strongly the old theory. Still the classification of Berzelius prevailed and was confirmed by H. Rose,‡ who showed the correspondence of the mole-

* "Schweigg. Journ. f. Ch. u. Ph.," xv, p. 296.
† "Pogg. Ann.," lvi, p. 101.
‡ "Pogg. Ann.," lxxiv, p. 429.

cular volumes of Be_2O_3 with Al_2O_3, and also by Ebelmen,[*] who obtained the oxide of beryllium in crystals isomorphous with Al_2O_3. Subsequently an elaborate work, " De Glucium et de ses Composées," 1855, by Debray,[†] once more caused a change in the prevalent opinion.

Debray regarded beryllia as an isolated member of the series occupying a position intermediate between the monoxides and the sesquioxides, and showing marked analogies with both groups, but not intimately connected with either of them by isomorphism. As the analyses of its compounds in most cases agreed better with the simple formula BeO, this was preferable to Be_2O_3.

Klatzo,[‡] in 1868, endeavoured to decide this matter finally by the assumption of a complete isomorphism between the sulphates of Be and Mg, Co, Fe, Ni, and though Marignac,[§] in 1873, proved that this pretended isomorphism did not exist, and was founded on a grave mistake, the opinion that beryllia was a monoxide was at this time universally accepted by chemists. Theoretically this opinion was founded on the " periodic law " of Mendeléeff.[||] The classification of beryllium at the head of the second group among the diatomic elements is a leading point in the theory of Mendeléeff.

If the composition of beryllia was Be_2O_3, and the atomic weight of beryllium $=13·8$, instead of $9·2$, the place of $Be = 9·2$ in the system would be vacant, and the order of the series partially reversed, the " atomic analogies " would be overthrown, and, still worse, beryllium $=13·8$ would find no place at all in the system, except in the fifth group among the five-atomic elements, to which it certainly does not belong.

The final decisive proof still wanting to confirm the ideas of Mendeléeff's was furnished, 1877, by Reynolds,[¶] who found the specific heat of metallic beryllium $=0·642$, which $(Be = 9·2)$ makes the atomic heat $= 5·9$, in accordance with the law of Dulong and Petit.

About a year before the publication of Mr. Reynolds, we had succeeded, by means of a new method, in isolating metallic beryllium from its chloride. We employed[**] a massive crucible of wrought iron, hermetically closed by a screw-plug, wherein equivalent quantities of beryllium chloride and metallic sodium were heated to redness. Metallic beryllium was thus obtained, partly fused into globules, partly forming aggregations of little prismatic crystals, which in brightness

    * " Ann. d. Ch. u. Pharm.," lxxx, p. 211.

    † " Ann. de Chimie et de Phys.," [3], xliv, p. 5.

    ‡ " Ueber die Constitution der Beryllerde."   Dorpat, 1868.   " Journ. f. Prakt. Ch.," cvi, p. 227.

    § " Ann. de Chim. et de Phys.," [4], xxx, p. 45.

    || " Ann. d. Ch. u. Pharm., Suppl.," viii, p. 151 (1871).

    ¶ " Phil. Mag.," [5], iii, p. 38.

    ** For the details of the experiment see " Darstellung und Valenz des Berylliums," " Pogg. Ann.," [2], iv, p. 554 (1878).

and colour resembled needles of polished steel. The metal was, as might be expected, not absolutely pure. The analysis was somewhat difficult, the mean result of a number of accordant determinations being :—

Be (metallic).............	86·94 per cent.
Be_2O_3	9·99 ,,
Fe	2·08 ,,
SiO_2	0·99 ,,
	100·00

We next determined its specific heat by the method of Bunsen (ice-calorimeter). We here met with quite unexpected difficulties; but, having given up the original arrangement of the experiment described by Bunsen [*] as impracticable, we, by means of an arrangement similar to that recommended by Schuller and Wartha,[†] obtained the following results :— [‡]

Specific heat of Be$=0·4084$ between 0° and 100°.

Atomic heat of Be$=5·64$ [Be$=13·8$].

These results, not in accordance either with those recently obtained by Mr. Reynolds or the periodic law of Mendeléeff, were not accepted without hesitation by chemists. Notwithstanding that, the editor of the new edition of Gmelin's "Handbuch d. Chemie," Professor Kraut, altered the formulæ of beryllia and its compounds in the part of the great encyclopædia of chemistry then passing through the press, several other chemists publicly or privately commented on our work, and urged us to pursue our inquiries further. Among the objections thus made we deem the following most worthy of discussion.

Mr. Lothar Meyer § hints that the equivalent of beryllium may be wrong, and suggests a revision of that number. If it should be found lower than 4·0, instead of higher, beryllium may still be considered a three-atomic element, without upsetting the periodic law. In that case it would only be necessary to interpose a new group of metals between the trivalent and quadrivalent elements. We had no reason to doubt the accuracy of the old number ($=4·6$), which we had found and verified by many analyses, but we redeemed our promise to Mr. Lothar Meyer,|| and undertook the following determinations of the atomic weight of beryllium.

In order to determine this value with the utmost accuracy, we thought it safest to choose the simplest possible method, viz., the

* "Pogg. Ann.," cxli, p. 1.

† "Pogg. Ann.," [2], ii, p. 359.

‡ *Obs.*—Allowance is made for the impurities of the metal. The specific heat of Be_2O_3 was found $=0·2471$ between 0—100° C.

§ "Ber. d. Deutsch. Chem. Gesellsch.," xi, p. 576.

|| *Ibid.*, p. 906.

analysis of its sulphate. Originally we also thought of analysing the chloride by titration with silver nitrate, but having found that sublimed beryllium chloride could not be obtained entirely pure, on account of its corrosive action on glass, we gave up the idea.

Sulphate of beryllium is undoubtedly a neutral salt, and is easily obtained in beautiful crystals, which do not change in the air ; but at 100—110° C. it loses half of its water, at 250° it becomes anhydrous, and after heating to light redness pure beryllia remains. Still there is a difficulty in the analysis ; for anhydrous sulphate and pure beryllia, as obtained by calcination, are both very hygroscopic substances. We therefore chose the hydrated sulphate, which could be weighed with the greatest accuracy, as the most fitting substance to start with ; this salt allowing pulverisation and pressure* without losing a trace of its constituent water. The sulphate was prepared by heating to dryness an aqueous solution of sublimed chloride with an excess of pure sulphuric acid. By repeated crystallisation the sulphate could easily be purified from a slight trace of calcium sulphate, originating from the action of the gaseous chloride on the glass tubes.

The analyses I, II, refer to beryllium sulphate obtained in this manner; for III, IV, the chloride was precipitated with ammonia and the hydrate treated with sulphuric acid. The sulphate was repeatedly crystallised. The difficulty in the analysis is the weighing of the calcined beryllia. For this purpose the crucible, still red hot, was placed in an exsiccator filled with anhydrous phosphoric acid, and after cooling placed immediately on the scale pan of a Bunge's balance, the equilibrium being beforehand approximately established. In this manner the whole operation required only a few seconds.

By spectroscopical test Professor Thalén has found the beryllia used for these determinations to be absolutely pure.

The hydrated beryllium sulphate has given in the determinations, thus executed, the following values :—

Experiment.	Weighed Sulphate.	Loss of water at 100° C.		Loss of water and SO_3.		Beryllia.		Equivalent of beryllium.	
	grs.	gr.	per cent.	grs.	per cent.	gr.	per cent.	$O = 8$	$O = 7·98$
I	3·8014	0·7696	20·245	3·2627	85·829	0·5387	14·171	4·556	4·544
II	2·6092	0·5282	20·244	2·2395	85·831	0·3697	14·169	4·552	4·542
III	4·3072	—	—	3·6973	85·840	0·6099	14·160	4·545	4·533
IV	3·0091	—	—	2·5825	85·824	0·4266	14·176	4·557	4·550
Mean	—	—	—	—	85·831	—	14·169	4·552	4·542

* It was pressed between sheets of fine, porous, bibulous paper, the surface of which had been previously smoothed by heavy pressure.

The equivalent of beryllium has hitherto been determined by—

Berzelius . . . . $=$ 4·9 . . . . . . (analysis of the sulphate).

Awdéeff . . . . $= \begin{cases} 4·71 \ . . . . . & \quad ,, \qquad ,, \qquad ,, \\ 4·93 \ . . . . . & \text{(analysis of the chloride).} \end{cases}$

Weeren . . . . , . . . $=$ 4·62 . . . . . (analysis of the sulphate).

Klatzo . . . . $=$ 4·59 . . . . .   ,,   ,,   ,,

Debray . . . . $=$ 4·61—4·71 (analysis of the oxalate).

Nilson and Pettersson $=$ 4·552. . . . . (analysis of the sulphate).

All these numbers are higher than 4·0, and consequently the atomic weight of beryllium, if trivalent, must be 13·65, consequently higher than that of carbon.   The before-mentioned supposition is consequently proved to be unfounded.

Mr. Lothar Meyer further observes that the atomic heat of the oxygen in beryllia, if a sesquioxide, would be less than in any other oxide known.   In the next paper we give the whole series of our determinations of the molecular heats of the rare earths and their sulphates.   From this survey, which shows that beryllia, with regard to heat and volume, occupies its proper place at the head of the sesquioxides, we here only extract a few determinations.*   If c signifies the specific heat,—

Atom. heat
of oxygen.

In Be_2O_3 $c=$ 75·32 . 0·2471=18·61
       Be_2 $c=$ 27·32 . 0·4246=11·60

$\overline{\hspace{2cm}}$

7·01=3.   2·34

,, Al_2O_3 $c=$102·8 . 0·1825=18·78
       Al_2 $c=$ 54·8 . 0·2143=11·74

$\overline{\hspace{2cm}}$

7·04=3.   2·35

,, Sc_2O_3 $c=$136·0 . 0·1530=20·81
       Sc_2 $c=$ 88·0 . 0·1454=12·80†

$\overline{\hspace{2cm}}$

8·01=3.   2·67

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* Our determinations refer to pure oxides obtained by chemical operations. They are also strictly corresponding and comparable.   Other determinations with native alumina (sapphire), made by different methods (Regnault, Neumann), gave a higher number.   Determinations by means of the ice-calorimeter always give smaller results, because the standard measure for the heat developed is greater (1 calory = mean of the specific heat of water between 0—100° C.).

† The atomic heat of scandium is supposed to be =6·4, according to the law of Dulong and Petit.

Atom. heat
of oxygen.

In Ga_2O_3 $c=$ 184 . 0·1062$=$19·54
Ga_2 $c=$ 136 . 0·0802$=$10·91
$$\overline{}$$
$$8·63=3.\quad 2·88$$

,, In_2O_3 $c=274·8$. 0·0807$=22·17$
In_2 $c=226·8$. 0·0570$=12·92$
$$\overline{}$$
$$9·25=3.\quad 3·08$$

According to the determinations made by us under identical con-
ditions, and therefore strictly comparable, the atomic heat of oxygen
in beryllia$=Be_2O_3$ is the same as that in alumina ; this, however, can
by no means be considered as exceptional. Alumina and beryllia are
the leading members of a group of sesquioxides, wherein the atomic
heat and (as will be seen from the following paper) the atomic volume
of oxygen increases with increasing values of the atomic weights of
the metals.

We will now refer to another objection raised to our former re-
searches. Mr. Brauner* admits the specific heat of beryllium to be
0·4084 between 0—100°, but supposes that it may rapidly increase
with the temperature in the same way as does the specific heat of
C and Bo. If this were the case, he thinks beryllia could be
BeO, the atomic heat of beryllium$=3·76$ between 0—100°, and
normal$=6·4$ first at a much higher temperature. In our detailed
paper, we have tried to meet such an objection, by pointing out that no
metallic element is as yet known, the atomic heat of which does not
agree with the law of Dulong and Petit. However, in order to remove
any doubt in this respect, we have determined the specific heat of
beryllium at different temperatures lying between 0—300° C. We
sifted the metal used in our former determinations through a gauze
of platinum, the holes of which were 0·25 sq. millim. For the
following experiments we used only that part which did not pass
through the gauze, on the supposition that this, consisting of globules
and larger crystals, was the purer metal. The analysis confirmed
this opinion, for the composition was found to be—

Beryllium . . . .   94·41
Beryllia. . . . .   4·89
Iron. . . . .   0·70
$$\overline{}$$
100·00

The following table gives only the results, not the details of our

* " Ber. d. Deutsch. Chem. Gesellsch.," xi, 1872.

determinations;* the values are referred to pure beryllium, making allowance for the impurities of beryllia and iron :—

Temperature.	Specific heat.	Atomic heat.	
0— 46·30 C.	0·3959		
0— 46·30	0·3950		$\Big\}$ 5·46	Heating in the vapour of CS_2.
0— 46·30	0·3980		
0— 46·50	0·4005		
0—100·18	0·4250	$\Big\}$ 5·79	Heating in the vapour of water.
0— 99·97	0·4242		
0—214·0	0·4749	$\Big\}$ 6·48	Heating in the vapour of nitrobenzol.
0—214·0	0·4751		
0—299·5	0·5054	$\Big\}$ 6·90	Heating in the vapour of diphenylamine.
0—299·5	0·5066		

Thus the specific and atomic heat of beryllium increase with the temperature, but a comparison with the same numbers for iron between 0—300° C. shows that such an increase of these values is not unusual.

	0—100°.		0—300°.		Authority.
	Specific heat.	Atomic heat.	Specific heat.	Atomic heat.	
Iron........	0·1124	6·29	0·1266	7·09	Bède.
Beryllium...	0·4246	5·79	0·5060	6·90	Nilson and Pettersson.

Between 0—100° C., the atomic heat of beryllium is equal to that of aluminium=5·87, and gallium=5·59, at 214° C. it is normal=6·48, and at 300° C. it has attained the same value as iron at the same temperature. Beryllium can thus certainly not be compared with the diamond in this respect, the specific heat of which, according to the researches of Weber, being many times higher at 0—300° C. than at 0—100° C.†

Every doubt as to the real atomic weight of beryllium must be

* We have also been obliged to determine the increase of the specific heat of beryllia and platinum by higher temperatures in the same way as that of beryllium itself, the metal for the experiments being enclosed in little capsules of platinum foil, hermetically soldered with chemically pure gold. Glass tubes cannot be employed at higher temperatures than 100° for two reasons : 1st, the glass would crack when suddenly cooled to 0° ; and 2nd, its specific heat increases very rapidly.

† " Ber. d. Deutsch. Chem. Gesellsch.," v, 303.

removed by the results above mentioned. Fixed at 13·65, according to our determinations, the value of its atomic heat becomes perfectly harmonious with the law of Dulong and Petit.

We will, in conclusion, say a few words upon a paper wherein the results of our former researches have been criticised. In the "Proceedings of the Royal Society," 1879, Mr. Carnelley applies a new method of calculating the fusion points of halogen compounds, and applying it to those of beryllium, argues in the following manner :—

Beryllium must be either a dyad or a triad, and must belong either to the second or to the third group of Mendeléeff's series ; if a dyad or $Be=9\cdot2$, its chloride, $BeCl_2$, can be calculated to fuse at $+547-$ $+600°$ C, which is confirmed by experiment; if a triad or $Be=13\cdot8$, the chloride, $BeCl_3$ or Be_2Cl_6, ought to fuse about 500 degrees lower, *i.e.*, at $+50°-+100°$ C., which it obviously does not ; *ergo*, beryllium is a dyad, and $Be=9\cdot2$.

We presume that Mr. Carnelley's knowledge of the physical properties of the triads is, like our own, very limited. With the exception of aluminium, we really know little or nothing of the melting or boiling points of chlorides, bromides, and iodides belonging to this group, and we think analogies taken only from one member, aluminium, to be too narrow a base for a calculation which is meant to apply to the whole group. There may be chlorides, bromides, and iodides which do not behave like Al_2Cl_6, in regard to boiling and fusion points. We will, in the following paper, give reasons for our opinion that beryllium and aluminium are each leading members of two different groups of trivalent metals. The nearest relatives of beryllium among these are neither calcium and magnesium, with which it has, in fact, little or nothing in common, nor aluminium, with which it has very much more in common, but rather the rare elements, scandium, yttrium, erbium, and ytterbium. We believe that Mr. Carnelley ought to try his calculation on the halogen compounds of the rare elements before asserting "that Nilson's and Pettersson's determination of the specific heat of beryllium must be incorrect." If the properties of the halogen compounds of these elements should be found to agree with the calculation, then we confess that the matter becomes somewhat uncertain, for then one will have to choose between the law of Dulong and Petit and that of Carnelley.*

Our above-mentioned experimental researches, confirmed still more by the experiments, which will be quoted in a second paper, lead us to the conclusion that the real atomic weight of beryllium is $=13\cdot65$. But with this value the periodic law cannot admit this element among the metals nearest related, and this fact obviously militates against its

* "Ber. d. Deutsch. Chem. Gesellsch.," v, 303.

general applicability.   Before concluding this memoir, we will just point out that this is not an isolated case of its kind.   For the element which should take its place between $Sb=122$ and $I=127$, the periodic law requires an atomic weight$=125$; with regard to its general properties tellurium is quite admissible in this place, but its atomic weight$=128$ is too high.   Although this number was the result of the determinations of Berzelius and v. Hauer, this want of accordance with the periodic law induced Willis* to make a new determination, but he only confirmed the former results.   Thus neither tellurium nor beryllium can be fitted into Mendeléeff's system.   And further, after Councler's† discovery of the boroxychloride, $BoOCl_3$, boron may be considered as five-atomic, but it certainly cannot be placed among elements of that valence ; and when once the chemistry of the rare earth-metals shall be made clear, where can be placed all these elements, the number of which has already become very great and doubtless will be still augmented ?   Already erbium and ytterbium, with the now fixed atomic weights of 166‡ and 173,§ for the pure metals (the earths$=Er_2O_3$ and Yb_2O_3), can scarcely be ranged in Mendeléeff's system in places indicated by their relation to the other earth-metals or by their " atomic analogies."

   In consequence of what has been indicated here, the periodic law in its present condition cannot be said to be quite an adequate expression for our knowledge of the elements ; this theory, however, having given the most striking proofs that the truth in many respects has been found (as for example : the new formulæ for the rare earths $=R_2O_3$ instead of RO, and the discovery of gallium and scandium, the existence of which the law has foreseen in the elements eka-aluminium and eka-boron), we may expect that the periodic law may be so modified and developed that it can embrace and explain every fact, stated by experiment.

* " Liebig's Ann. d. Ch.," ccii, p. 242.
† " Ber. d. Deutsch. Chem. Gesellsch.," xi, p. 1108.
‡ According to Cleve.
§ According to Nilson.